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Kinetic energy releases upon dissociation of endohedral fullerene cations

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Abstract

Kinetic energy release distributions are reported for the emission of C_2 from the positive ions of C_{60}, $Ne@C_{60}$, C_{82} and $La@C_{82}$. Finite heat bath theory was applied to deduce the C_2 binding (vaporization) energies, ΔE_{vap}. The results obtained are: $\Delta E_{vap}(C_{60}^+) = 7.1 \pm 0.5$ eV, $\Delta E_{vap}(Ne@C_{60}^+) = 7.4 \pm 0.5$ eV; $\Delta E_{vap}(C_{82}^+) = 6.1 \pm 0.4$ eV and $\Delta E_{vap}(La@C_{82}^+) = 7.3 \pm 0.4$ eV. The endohedral neon atom has a minor effect on the cage binding, while lanthanum has a relatively strong effect.

1. Introduction

The fullerenes are closed cages with cavities large enough to contain atoms. Evidence that metal atoms can combine with arc-vaporized carbon atoms to form endohedral metallofullerene molecules [1] was reported shortly after the discovery of fullerene molecules [2]. The groups at Rice [3] and IBM [4,5] developed techniques to produce metallofullerenes in bulk by laser- or arc-vaporization of graphite–metal composites in helium. Schwarz and co-workers were the first to demonstrate [6–8] the inclusion of noble gas atoms within C_{60}^+ and C_{70}^+ through high-energy collision experiments. Neutral fullerene–noble gas compounds, $He@C_{60}$ and $Ne@C_{60}$ first [9] and argon, krypton and xenon compounds later [10], were prepared by Saunders and co-workers. This was achieved by heating the fullerenes at 600°C under high pressures of the noble gases.

In contrast with other molecules that bind ligands through noncovalent forces, the fullerenes are like closed bottles. Atoms or small molecules can be contained and held without need for binding interactions [9]. Theoretical calculations [11] indicate that the Ne endohedral complex is slightly destabilized while complexes with ions are strongly stabilized. Furthermore, endohedral complexes with metals such as La are predicted [12] to be composed of the metal cations situated off-center and a negatively charged fullerene cage. EPR studies of lanthanum-containing C_{82} [4] have revealed that the lanthanum atom has a formal charge of 3 + and the C_{82} a charge of 3 − . Clearly the bonding in $La@C_{82}$ is quite different from that in $Ne@C_{60}$.

Fullerenes, as well as endohedral fullerenes, undergo C_2 evaporation reactions. The C_2 binding energy to the fullerene cage can be determined through modelling of experimental kinetic energy

release distributions (KERDs) for the elimination reactions [13–17]

$$C_n^+ \rightarrow C_{n-2}^+ + C_2. \tag{1}$$

An endohedral atom which is 'bottled' in the cage and only weakly bound should have a negligible effect on the C_2 binding energy and on the kinetic energy release (KER) upon C_2 evaporation. However, strong binding of the endohedral atom might affect the cage and therefore the C_2 binding energy and the KER upon evaporation.

We report here on KERDs for C_2 evaporation from C_{60}^+, C_{82}^+ and from the endohedral ions $Ne@C_{60}^+$ and $La@C_{82}^+$. C_2 binding energies will be deduced and the effect of the endohedral atom on the binding of the cage will be determined.
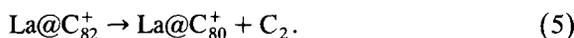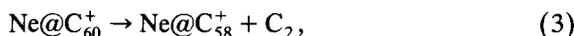
2. Experimental description

The experimental methods for determining the KERDs have been described previously [17]. Measurements were performed on a high-resolution double-focusing mass spectrometer of reversed geometry, the VG-ZAB-2F [18,19]. The $Ne@C_{60}^+$ and $La@C_{82}^+$ ions were obtained by ionization of the corresponding neutral samples, which were prepared by the methods described previously [4,9].

The samples were introduced into the mass spectrometer using the direct insertion probe. The electron-impact conditions were as follows: electron ionizing energy, 70 eV; emission current 5 mA; source temperature 400°C; and resolution, 1100 (10% valley definition). Metastable ion peak shapes were determined by scanning the electrostatic analyzer and using single-ion counting. Ion counting was achieved by a combination of an electron multiplier, amplifier/discriminator, and multichannel analyzer [20]. The experiments were performed at 8 kV accelerating voltage and main beam widths ranging from 1 to 11 V. The metastable ion peak shapes obtained were mean values of 500–2200 accumulated scans. This was done in a computer controlled experiment, monitoring the main beam scan and correcting for the drift of the main beam [19]. The product KERDs were determined from the first derivatives of the metastable ion peak shapes [21–23], with deconvolution of the main beam distribution. The KERDs

deduced were found to be independent of the energy resolution employed within the range described above.

3. Results and discussion

Metastable peak shapes were determined for the reactions

$$C_{60}^+ \rightarrow C_{58}^+ + C_2, \tag{2}$$

$$Ne@C_{60}^+ \rightarrow Ne@C_{58}^+ + C_2, \tag{3}$$

$$C_{82}^+ \rightarrow C_{80}^+ + C_2, \tag{4}$$

$$La@C_{82}^+ \rightarrow La@C_{80}^+ + C_2. \tag{5}$$

The center-of-mass product KERDs for reactions (2) and (3) are given in Fig. 1 and for reactions (4) and (5) in Fig. 2.

The unimolecular decompositions (2)–(5) may be viewed as evaporations from small particles. This process has been treated theoretically by Klots [14,24]. It has been proposed that the average kinetic energy with which a monomeric unit leaves the surface of an aggregate can measure the temperature of the transition state, $T^{\ddagger}$. This idea was developed further by Klots [14,24] treating the full KERD. In the model-free approach the KERD is written in the form

$$p(\epsilon) \approx \epsilon^l \exp(-\epsilon/k_B T^{\ddagger}), \quad 0 \leqslant l \leqslant 1, \tag{6}$$
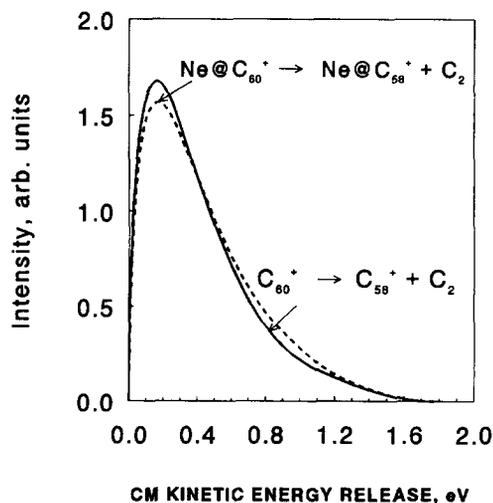

Fig. 1. Experimental center of mass kinetic energy release distributions. (——) reaction (2); (– – –) reaction (3).
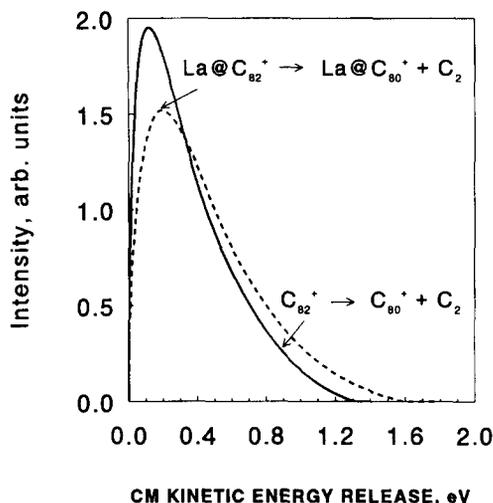
Fig. 2. Experimental center of mass kinetic energy release distributions. (——) reaction (4); (– – –) reaction (5).

where ϵ is the kinetic energy, k_B is Boltzmann's constant, T^+ is the transition state temperature, and l is a parameter. The KERDs for all of the reactions studied could be fitted by expression (6). The parameters l and T^+ were deduced and are summarized in Table 1. Once T^+ is extracted from the KERD, T_b may be calculated from [25]

$$T_b = T^+ \frac{\exp(\gamma/c) - 1}{\gamma/c}, \qquad (7)$$

where T_b is the isokinetic temperature to which a heat bath must be set to yield a thermal rate constant $k(T_b)$ equal to the microcanonical rate coefficient, $k(E)$, characteristic for the cluster decomposition; γ is the universal Gspann parameter, $\gamma = 23.5 \pm 1.5$ [26] and c is the cluster heat capacity in units of k_B

Table 1
Parameters obtained in this study

	C_{60}^+	$Ne@C_{60}^+$	C_{82}^+	$La@C_{82}^+$
$\bar{\epsilon}$ (eV)	0.44 ± 0.01	0.44 ± 0.02	0.37 ± 0.02	0.46 ± 0.02
l	0.55	0.56	0.51	0.6
$k_B T^+$ (eV)	0.278	0.294	0.247	0.294
$k_B T_b$ (eV)	0.30	0.317	0.261	0.309
ΔE_{vap} (eV)	7.1 ± 0.5	7.4 ± 0.5	6.1 ± 0.4	7.3 ± 0.4

minus 1. The cluster vaporization energy ΔE_{vap} is calculated from Trouton's rule [14,24–28],

$$\frac{\Delta E_{vap}}{k_B T_b} = \gamma. \qquad (8)$$

The values of T_b and ΔE_{vap} extracted from the experimental KERDs are included in Table 1. The vaporization energies are equal to the ionic C_2 binding energies in the absence of a reverse activation energy term.

Several interesting results transpire: (1) The C_2 binding energy of $Ne@C_{60}^+$ is the same as for C_{60}^+ within experimental error. The neon endohedral atom does not affect the cage binding. (2) The C_2 binding energy of $La@C_{82}^+$ is about 1 eV higher than for C_{82}^+. The lanthanum endohedral atom has a strong effect on the cage binding. (3) The C_2 binding energy of C_{82}^+ is ~ 1 eV lower than for C_{60}^+. (4) The C_2 binding energy deduced for C_{60}^+ is in agreement with recent results [29] (7.1 ± 0.4 eV) based on comparison between measured and calculated breakdown curves. Earlier results based on KERDs from this laboratory [17] gave a lower binding energy of 5.23 eV for two reasons. First, the average kinetic energy deduced was too low (0.362 eV); recent values which we have measured over the last year are all 0.44 ± 0.01 eV, in agreement with our earliest measurements [15] and we are quite certain of this value. Secondly, the model free approach adopted here gives binding energies which are about 1 eV higher than by application of the spherically symmetric potential model [17]. Recent extensions [30] of the spherical symmetric potential approach, which include more terms in the potential, raise the values of the derived binding energies. Thus, while the absolute C_2 binding energy in C_{60}^+ may be as high as 7.6 eV [31] the relative values deduced in this work are still correct, namely: $\Delta E_{vap}(C_{82}^+) < \Delta E_{vap}(C_{60}^+) \approx \Delta E_{vap}(Ne@C_{60}^+) \approx \Delta E_{vap}(La@C_{82}^+)$.

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